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Spotlights on Recent *JACS* Publications

PREDICTING GAS STORAGE CAPACITY OF METAL–ORGANIC FRAMEWORKS

Among alternative energy fuels, natural gas is gaining popularity. However, methane, the major component of natural gas, is notoriously hard to liquefy and transport, and the process is also incredibly energy inefficient. It is more effective to instead adsorb methane molecules into porous materials that have very high surface areas. These crystalline metal–organic frameworks (MOFs) are known to have high storage capacity for methane, but current technologies do not yet meet U.S. Department of Energy adsorption standards. Scientists are searching for better storage materials, and the ability to determine the methane absorption capacity of a designed MOF structure prior to synthesis would be a tremendous advantage.

In a step toward this goal, Joachim Sauer and Kaido Sillar used computational analysis to determine the gas adsorption abilities of a type of magnesium MOF known as CPO-27-Mg (DOI: 10.1021/ja307076t). They studied methane adsorption onto different sites in the Mg MOF and found that interactions between the adsorbed molecules increased the adsorption energy by 10% and the adsorption capacity by 15%, based on how full the MOF is. They could also determine differences between perfectly crystalline and slightly defected MOFs, showing that their calculations are highly accurate. This use of theory to predict adsorption behavior of MOFs may help advance methane storage and transportation technologies, leading to potential alternative energy technology in the future. **Leigh Krietsch Boerner, Ph.D.**

TWEAKING MONOLAYERS FOR EVEN BETTER LITHIUM ION BATTERIES

The storage capacity of lithium batteries depends directly on the amount of lithium ions that can be included in the electrodes. Graphene, a two-dimensional hexagonal material consisting of single sheets of carbon atoms, has been extensively investigated as an anode material. Because of the limitations of graphene—its chemical and electrical properties cannot be tuned—researchers are also investigating other 2-D materials composed of atomic species other than just carbon.

Carbide and carbonitride nanosheets are a class of such alternative monolayer materials. Because they have a hexagonal structure and properties comparable to those of graphene, they are termed MXenes. Expecting that such 2-D materials might be suitable for anodes in lithium ion batteries, Zhen Zhou and co-workers investigated Ti_3C_2 monolayers and their fluorinated and hydroxylated surfaces, $Ti_3C_2F_2$ and $Ti_3C_2(OH)_2$, respectively (DOI: 10.1021/ja308463r). Applying density functional theory, their computer models confirmed their hunch: besides good electric conduction and fast Li ion adsorption and desorption rates, the amount of Li ions that MXenes can adsorb is quite impressive. Ti_3C_2 layers can store up to one Li ion per carbon atom, which compares favorably with the storage capacity of one Li ion per six carbon atoms for pure graphite. **Alexander Hellemans**

MAPPING A RADICAL REACTION

Superoxide, a free radical derived from oxygen but with an extra electron and a negative charge, readily reacts with many biological molecules found in cells such as proteins and nucleic acids. Sometimes such oxidation harms cells, though the mechanism often remains a mystery. Researchers have hypothesized that the products of reactions between superoxide and tyrosyl radicals, another common intracellular radical, further add to the damage. Now researchers have completely characterized the products of that proposed reaction.

Ned Porter and colleagues generated superoxide in the presence of different types of tyrosyl radicals (DOI: 10.1021/ja307215z). They report that the stable products are forms of hydroperoxide and hydroxyl derivatives of the tyrosine. The team then used chromatography, mass spectrometry, and nuclear magnetic resonance spectroscopy to examine the structures of the products in detail. They found that the superoxide most often modifies the original tyrosine at the *para* position. The so-called *para* finding is a surprise, since most other radicals react more readily at the alternative *ortho* site. The authors suggest that substitution at the *para* site may make the new tyrosine-derived products more reactive in biological systems. **Lucas Laursen**

SINGLE-MOLECULE STUDY UNTANGLES ALZHEIMER-ASSOCIATED PROTEIN AGGREGATES

Numerous neurodegenerative disorders—specifically "tauopathies", including Alzheimer's disease—are characterized by aggregation of a protein called tau in the brain. Still unresolved is how tau transitions from disordered, otherwise soluble molecules in healthy individuals to protein tangles in the disease state. Using single-molecule Förster resonance energy transfer (FRET), Shana Elbaum-Garfinkle and Elizabeth Rhoades have begun to tease apart the answer (DOI: 10.1021/ja305206m).

The team prepared a dozen tau constructs, each containing a FRET donor–acceptor pair at defined positions across the molecule. They then analyzed the efficiency of donor–acceptor energy transfer to probe the molecules' structures in solution in the presence and in the absence of heparin (a polyanion that induces protein aggregation) or salt.

Based on FRET efficiency data, the authors developed a model of tau in which the protein is relatively compact in solution, with its N- and C-termini in close proximity both to each other and to an internal microtubule-binding domain. In the presence of heparin, the microtubule-binding domain contracts while the termini separate, suggesting a protein that is more structured centrally but flanked by regions that are more strung out.

The resulting heparin-bound conformation, the authors suggest, could prove useful to drug and diagnostics developers alike. "Stabilization of native long-range interactions may prove to be a successful strategy for preventing tau aggregation in

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Alzheimer's disease and tauopathies in general," they write. **Jeffrey M. Perkel**

DUAL OPTICAL NANOSENSOR MEASURES INTRACELLULAR PH AND OXYGEN

Oxygen concentration and pH are key indicators of cell health, metabolism, and physiology. Intracellular sensors for both parameters exist, yet they are limited: They can measure either pH or oxygen, but not both. Now Otto Wolfbeis and colleagues describe a new nanosensor that can quantify both oxygen and pH simultaneously, and do so inside living cells (DOI: 10.1021/ja308830e).

The nanosensor is a complex structure built from a hydrophobic polymer that is capped at either end with hydrophilic polyethylene glycol and a pH-sensitive fluorophore. The silica-coated core of the particle contains a reference dye and a porphyrin-based oxygen sensor. The resulting 12-nm particle is stable over long periods at 4 °C and is monodispersed in solution. As pH increases, the sensor's fluorescence likewise rises. Independently, as oxygen concentration goes up, the signal from the porphyrin oxygen sensor falls. Significantly, these nanoparticle sensors can be delivered into eukaryotic cells via transfection but do not cross cell membranes on their own, meaning they can be used to monitor physiology either within cells or outside of them.

"This new kind of nanomaterial enables, for the first time, confocal imaging of these two important parameters with very high resolution, even possible with nanometer resolution using nanoscopy," the authors conclude. **Jeffrey M. Perkel**

NITROGEN-ARMED NANOPARTICLES MAY IMPROVE BIOFUELS

Lignin, which together with cellulose provides plants their structural support, makes a tempting target as a renewable energy source because it is abundant and readily available. Yet its complex structure makes it difficult to convert using conventional catalysts.

Yong Wang and colleagues at Zhejiang University in China have created a new palladium nanoparticle-based hydrodeoxygenation catalyst that outperforms conventional catalysts in terms of selectivity and conversion efficiency (DOI: 10.1021/ja308139s). One innovation was to use nitrogen-doped carbon supports in the catalyst. The nitrogen, which the team applied using an ionic liquid, improved properties of the catalyst such as its capture of the palladium nanoparticles. The new catalyst converted all of the researchers' model lignin, vanillin, into a biofuel precursor, and performance was not diminished after six cycles.

The new catalyst is also environmentally friendly. When the team tested the new catalyst in water—a benign solvent—at low temperatures and pressures, they found that it worked as well as at higher temperatures, reducing the energy requirements of any future system which uses this catalyst. **Lucas Laursen**